The Total Heat of Liquid Carbonic Acid.

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The measurements described in the following paper were made at the request of the Engineering Committee of the Food Investigation Board, who requested the author to measure the total heats of CO_2 at pressures and temperatures above the critical point. These total heats may be read from the I ϕ chart published in a former paper,* but the part of the chart concerned is based on an unverified assumption, viz., that the specific heat at constant vol., C_v, is constant and equal to 0·214, and it was considered advisable to check its accuracy by direct measurements.

The measurements of the total heats were made in the same manner as those described in the former paper; the carbonic acid being pumped round a circuit at a uniform measured rate and heated through various ranges of temperature in an electrical calorimeter. Much of the apparatus was the same as had been previously used, but an improved calorimeter was used and several modifications were required to enable the measurements to be made at the higher temperatures and pressures required.

The general arrangement of the apparatus is shown in fig. 1. P is a motor-driven compressing pump. C is a gas cushion to reduce the shock and keep the flow more nearly uniform; it consists of a steel pipe heated at the top in a hot-water vessel. D is a cooling coil to reduce the temperature of the CO_2 to a steady temperature before it enters the calorimeter. E is the calorimeter described below. F is a water-cooled condensing coil. G,G, are two flasks, one hung on a steelyard which turns with 1/100 lb. and rings a bell when the lever falls; the other is used simply as a container. During a test the valves on the flasks are set so that CO_2 flows out of the weighing flask, through the pump and calorimeter and into the container. As each 2 lb. of CO_2 leaves the weighing flask the steelyard lever falls and rings the bell; a 2 lb. weight is then hung on the flask thus raising the lever again. When the test is finished the valves are reversed and the CO_2 pumped back into the weighing flask. During the preliminary adjustment, before the actual test begins, the valves are set so that the CO_2 circulates through the weighing flask (which is full). H is a standard pressure gauge graduated to 10 lb. per square inch and capable of being read to 2 lb. per square inch. It is connected through a coil of small pipe in a hot-water vessel which acts as a cushion to steady the

* 'Phil. Trans.,' A, vol. 215, p. 368.

needle. The rate of flow of the liquid to the pump is controlled by the two valves V_1 and V_2 in series. The pressure gauge, J, indicates the pressure between the valves, and the pressure gauge, K, indicates the pressure on the suction side of the pump. The two valves enabled the rate of flow to be

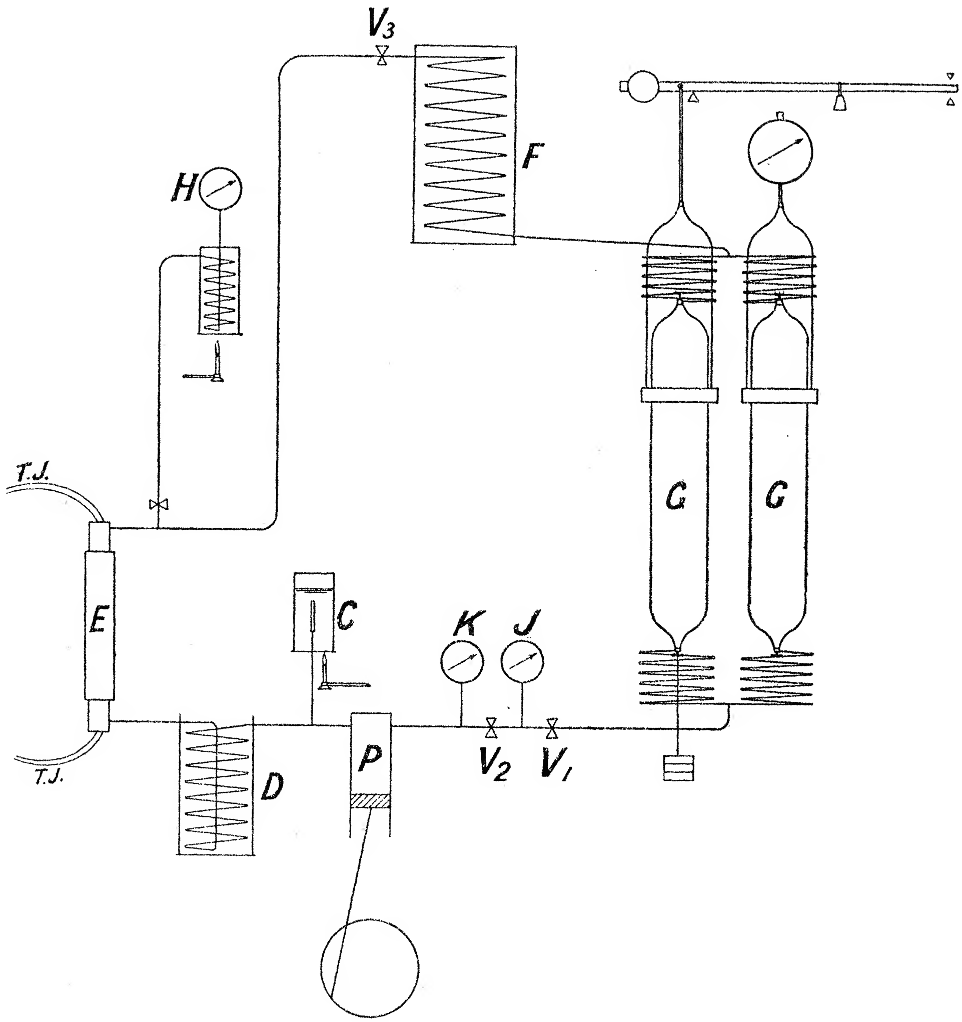

Fig. 1.

controlled much more accurately than it could with a single valve; during a test the valve V_2 was not touched and small adjustments were made on V_1 so as to keep the pressure, shown by gauge J, constant. The pressure in the calorimeter is controlled by the valve V_3 and read on the gauge, H.

The cycle of operations on the $I\phi$ chart is shown in fig. 2. The condition

of the liquid coming from the weighing flask is shown at "a." It expands through the throttle valves V_1 and V_2 to a pressure of about 200 lb. per square inch and is then in condition "b." It is then compressed adiabatically to the desired pressure, say 1,800 lb. as shown at "c." It is cooled in the coil, D, to about 12° C., to the point "d." It is then heated to the desired

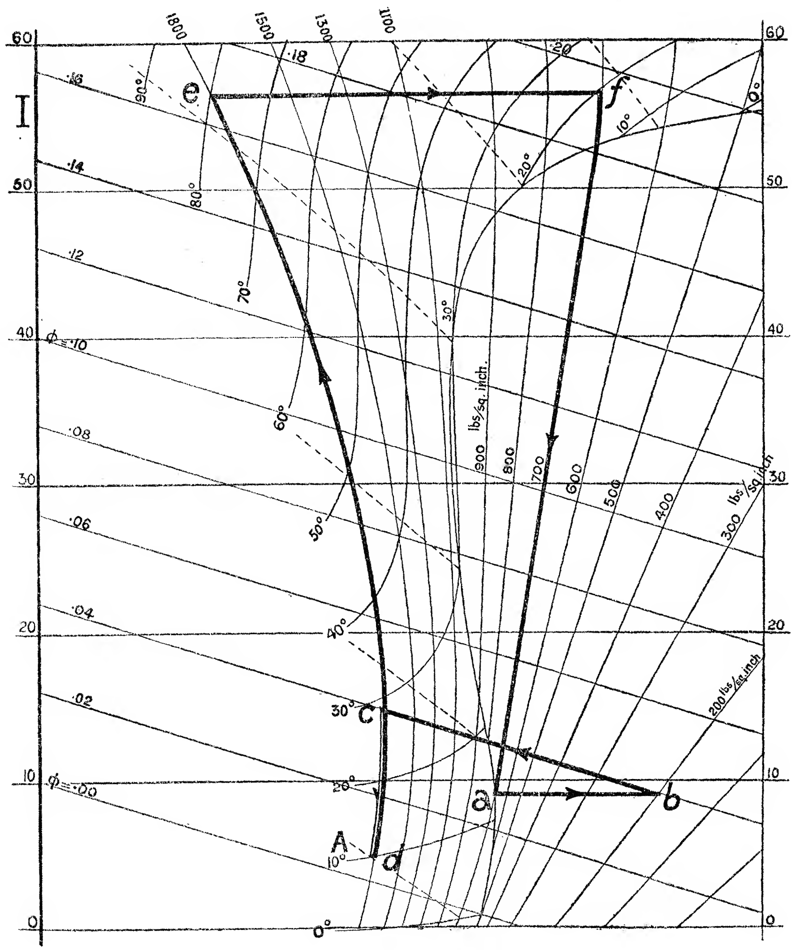

FIG. 2.—Part of I ϕ chart near the critical point.

temperature, to the point "e," in this diagram 80° C. It is then throttled through valve V_3 to the point "f," and cooled in the condensing coil, F, to the starting point "a." The total heat measured is shown on the chart by the vertical height between "d" and "e."

The calorimeter is shown in fig. 3. It consists of an outer steel tube, capable of standing the maximum pressure used, inside which is a bakelite

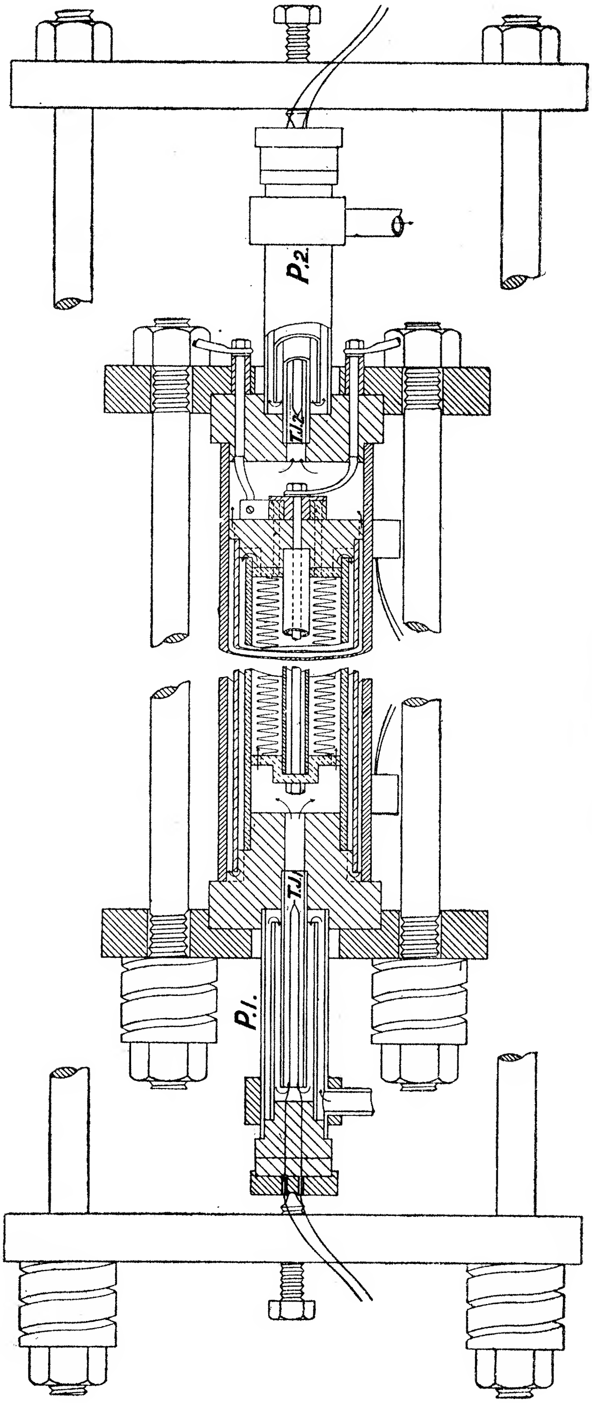

Fig. 3.—Calorimeter.

tube, and inside this again a fused silica tube. In the centre is a group of six nichrome steel-wire heating coils lashed round a small silica tube which supports them. The electrical connection to the one end of the heating coils passes through the central silica tube. The entering CO_2, which is at about atmospheric temperature, passes first along the outer space just inside the steel tube; it then returns along the space inside the bakelite tube, and finally passes down inside the silica tube, and is heated by the wire coils. By this arrangement the temperature of the outer steel tube is kept low, and radiation losses almost eliminated.

The CO_2 enters and leaves the calorimeter by two similarly arranged self-jacketed pipes, p_1 and p_2, enclosing the thermo-junctions, TJ_1 and TJ_2, which measure the temperatures before and after heating. The ends of the calorimeter were first made of hard vulcanite, but this softened at about 70° C., and vulcanite had to be abandoned for the hot end; a disk of bakelite was substituted, and answered admirably.

The thermo-junction wires were originally taken through the ends of the entering and outgoing pipes in the manner described in the former paper. A small button of brass was soldered on the wire; this was drawn through a thin rubber tube, which in turn was drawn into a conical hole in the vulcanite plug, as is shown in fig. 4. This arrangement was found to last only for a few hours, under the higher pressures, before the rubber tube failed. A new design, shown in fig. 5, was then tried; it consists of a small brass bolt with conical head through the centre of which the wire passes, being soldered into it. This formed a tight joint and appeared to

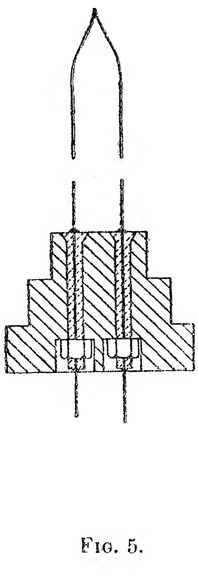

Fig. 5.

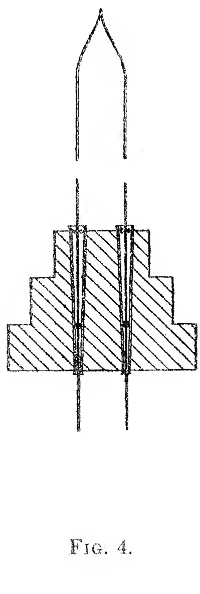

Fig. 4.

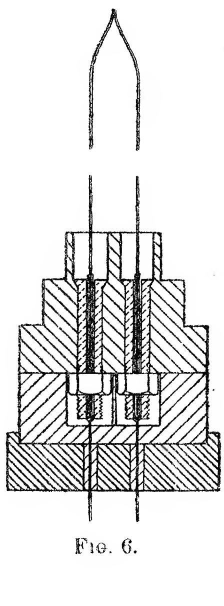

Fig. 6.

be satisfactory, but fortunately, a discrepancy in temperature readings, referred to below, called attention to a serious error which this bolt introduced. It will be noticed that the bolt virtually "short-circuits" a short length of the eureka wire; this has no effect unless there is a temperature gradient in the wire at that place, but if there is a temperature gradient it has the effect of reducing the temperature reading by approximately the difference of temperature between the two ends of the bolt. In other words, the use of the bolt is nearly equivalent to the introduction of an equal length of copper-wire in the eureka lead, which will give an opposing E.M.F., due to the difference in temperature between its two ends. This point was fully investigated by making a series of bolts of different lengths and soldering them on one of the wires of a thermo-junction a few inches apart and then calibrating the junction in an oil bath. No error was introduced except when the bolt was near the surface of the oil, *i.e.*, where there was a large temperature gradient in the wire, and then the error was roughly proportioned to the length of the bolt. The actual error will depend on many factors, but to show its importance the following may be quoted. The error was 3° C. for a bolt 20 mm. long in an oil bath at 40° C., the cold junction being about 10°, *i.e.*, the error was about 10 per cent. of the temperature difference.

The first method adopted for eliminating the error was to solder the bolt at one end only and to insulate the rest of its length from the wire. This, on trial, was found to be only partially successful, and further investigation showed that the thin layer of solder used to "tin" the wire was sufficient to cause a serious effect. Finally, the wire was coated with glue and black-lead to prevent the "tinning" from spreading, and a very short length cleaned and soldered to the bolt, the rest of the bolt being insulated from the wire by three layers of cigarette paper, shellac'd on (as shown in fig. 6). This proved perfectly effective. This small difficulty has been described at length because the presence of the errors may be so easily overlooked; it is purely a matter of chance whether it is found when the thermo-junction is calibrated.

The inlet and outlet temperatures were measured by the above-mentioned eureka-copper thermo-junctions and a potentiometer. The junctions were calibrated against a standard thermometer calibrated at the N.P.L., and a calibration curve plotted to a large scale.

The body of the calorimeter is surrounded when in use with a 2-inch cork jacket, given for this research by the Anglo Delta Slab Company. The temperature of the steel tube is measured by two Hoskin's alloy thermo-junctions, one at each end. A radiation test was made on the

calorimeter, and showed that the loss of heat was 7·46 watts when the temperature difference between the steel tube and the air outside the cork jacket was 26° C. The maximum correction in any experiment for radiation was only 0·85 per cent. of the measured heat.

The electrical power supplied to the calorimeter was taken from the town mains (100 volt. D.C.) and regulated by adjustable resistances in series with the heating coils. It was measured by means of a Siemens precision wattmeter, having two ranges of current and three ranges of voltage. The wattmeter is divided into 150 divisions, and can be read to 1/10 division. The wattmeter was calibrated against standard resistances and cadmium cells which had been freshly calibrated by the N.P.L. Fluctuations in the town voltage gave considerable trouble; it was found necessary to watch the wattmeter continuously and make fine adjustments as required to keep the power constant.

Preliminary trials showed that it would not be possible to keep the conditions of a test steady without some indicator showing the upper temperature to which the CO_2 was being heated in the calorimeter. A Hoskin's alloy thermo-junction was therefore tied to the outlet pipe and connected to a millivoltmeter, but this was found not to be sensitive enough. To increase the sensitiveness the thermo-junction was connected to a d'Arsonval galvanometer, the "cold junction" being put into a well-jacketed tank of water which was heated to and kept at the temperature to which it was desired to heat the CO_2. This differential arrangement answered admirably. The galvanometer gives a deflection of 125 mm. per degree centigrade (the whole 500 mm. scale corresponding to 4° C.). A paper scale marked in half degrees in bold figures was used, which could be seen across the laboratory and enabled all the four observers to see any variations which occurred in the top temperature. It was a disagreement between this indicator and the temperature given by the potentiometer which called attention to the serious error (which has been already described) introduced by the bolts in the thermo-junction leads.

The tests were carried out in the following way. The jacketed tank containing the cold junction for the indicator was heated to the temperature at which the test was to be run. The pump was started and the pressures approximately adjusted. The current was switched on to the heating coils in the calorimeter, and adjusted so that the power was about that estimated to give the required rise of temperature when the rate of flow of CO_2 was 1 lb. per minute. The rate of flow was then adjusted by closing the valve V_2 till the temperature reached the desired point, as shown by the

indicating galvanometer. After running for a short time, to allow all the conditions to get steady, the test was started.

During the test, readings were taken every minute of the following quantities: inlet temperature (potentiometer), outlet temperature (potentiometer), electrical power, outlet pressure.

The two jacket temperatures were read two or three times during a test. The times were noted when the bell rang, indicating the completion of each 2 lb. of CO_2. The total quantity of CO_2 passing through the calorimeter during a test was usually 20 lb.

The tests at the lower temperature were run at rates of about 1 lb. per minute, but at the higher temperature this rate had to be reduced, to prevent surging, shown by periodic variations of pressure and temperature. A slight increase of rate of flow has two effects. (1) A *lowering* of the final temperature, owing to the increased quantity to be heated. (2) A raising of the pressure, which reduces the value of I per pound, and consequently produces a *rise* of the final temperature. When the second effect is the larger the temperature rises, and the CO_2 expands, thus further increasing the pressure, and the condition is unstable. Considerable skill was required in manipulating the valves, to avoid periodic fluctuations due to this instability. At high rates the period of the fluctuations was too fast to control, but at lower rates it could be controlled satisfactorily.

Measurements were made at 900, 1000, 1100, 1200, 1300, 1500, and 1800 lb. per square inch pressure between temperatures of about 12° C. and 100° C. The results, after reduction, are shown by the dots in fig. 7. Smooth curves have been drawn through the points, and curves interpolated for 1400, 1600, and 1700 lb. per square inch. The values of the total heat for every 5° C. for each of the above pressures, taken from the curves, are given in the following Table. The observations at the higher temperatures are not quite as accurate as it was hoped to make them. The inaccuracy was due to the difficulty in keeping the top temperature steady. Repeated attempts were made to get steadier conditions by varying the rate of flow and by modifying the way in which the variations in the E.M.F. of the town supply were allowed for, but it was not found possible to get entirely satisfactory results.

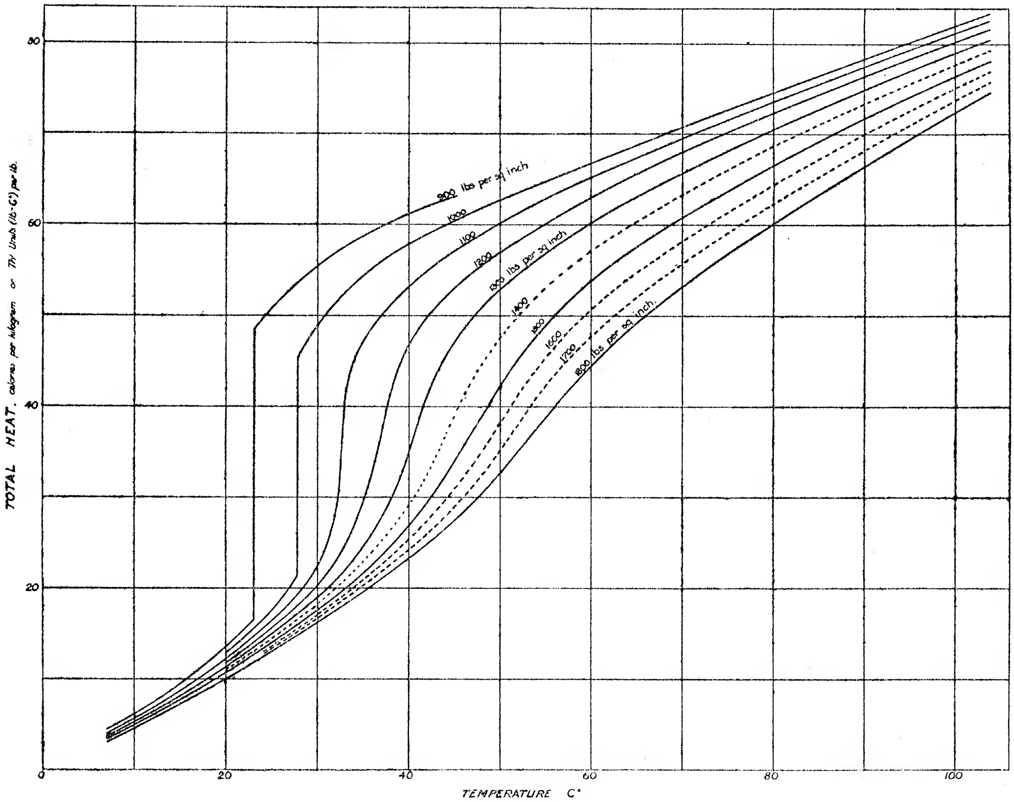

Fig. 7.

Total Heat I of CO_2 (Calories per kg. or lb. C.° per lb.).

Temp. ° C.	Pressure lb. per sq. in.									
	900	1000	1100	1200	1300	1400	1500	1600	1700	1800
0	0·34	0·23	0·14	0·06	—	—	—	—	—	—
5	3·21	3·05	2·90	2·77	2·64	2·55	2·47	2·38	2·29	2·19
10	6·16	5·92	5·70	5·51	5·34	5·19	5·02	4·89	4·75	4·60
15	9·5	9·1	8·8	8·5	8·2	7·9	7·7	7·5	7·3	7·2
20	13·5	12·9	12·3	11·8	11·4	11·0	10·7	10·4	10·2	10·0
25	50·8	17·5	16·4	15·6	15·0	14·4	14·0	13·6	13·4	13·1
30	55·4	48·9	22·4	20·2	18·9	18·3	17·5	17·1	16·7	16·2
35	58·6	54·4	47·3	29·7	24·6	22·9	21·6	20·8	20·2	19·7
40	61·1	57·8	53·2	46·9	35·1	29·2	26·8	25·4	24·2	23·3
45	63·1	60·4	57·1	53·1	47·2	39·2	34·1	31·0	28·9	27·4
50	—	62·8	60·2	56·9	52·9	47·6	42·2	38·3	35·2	32·7
55	—	64·7	62·9	60·1	56·8	53·1	48·9	45·4	42·3	38·9
60	—	66·8	65·2	63·0	60·2	57·1	53·9	50·8	47·7	44·5
65	—	68·8	67·4	65·6	63·1	60·3	57·6	54·8	52·0	49·3
70	—	70·8	69·5	68·0	65·7	63·3	60·8	58·2	55·7	53·2
75	—	72·7	71·5	70·2	68·2	66·1	63·8	61·5	59·1	56·8
80	—	74·6	73·6	72·3	70·6	68·7	66·6	64·4	62·3	60·1
85	—	76·5	75·6	74·4	72·8	71·0	69·3	67·3	65·3	63·3
90	—	78·4	77·5	76·4	74·9	73·4	71·8	70·0	68·2	66·5
95	—	80·2	79·4	78·3	77·0	75·6	74·1	72·6	71·0	69·5
100	—	82·0	81·2	80·2	79·0	77·7	76·4	75·1	73·7	72·4

Comparing the results with the $I\phi$ chart, published in the former paper (*loc. cit.*), it will be found that the chart gives slightly too low results, the largest error being in the left-hand top corner. The following examples will show the extent of the differences :—

Pressures.	100° C.	70° C.	40° C.
	per cent.	per cent.	per cent.
1800..............	7·0	6·7	4·2
1100..............	4·6	3·4	4·1
900..............	—	—	2·5

The results show that both the pressure lines and temperature lines require to be slightly shifted in the chart.

The results of the present investigation, combined with those in the author's last report,* are theoretically sufficient for the evaluation of the specific heat at constant volume, C_v, which has hitherto been assumed to be constant, as stated at the beginning of this paper. It is not easy to deduce from the data very accurate values for C_v, but the calculations appear to show that they are far from constant. This point is being further investigated, as it appears to be of considerable theoretical interest.

* 'Roy. Soc. Proc.,' A, vol. 98 (1920).

The Energy Involved in the Electric Change in Muscle and Nerve.

By A. V. Hill, F.R.S.

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By J. Joly, Sc.D., F.R.S.

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